

REMARKS/ARGUMENTS

Reconsideration of this application is requested. Claims 1, 2, 5, 9 and 11 remain active in the application subsequent to entry of this Amendment.

Restriction was required and the undersigned elected the subject matter of Group I, namely claims 1, 2, 5, 9 and 11, the only claims remaining in the case. The non-elected claims have been canceled, this action being taken without prejudice to divisional applications directed to the subject matter of these claims.

The claims have been amended in order to more particularly point out and distinctly claim that which applicants regard as their invention. Claim 1 is amended to define a sphericity in the range of 0.1 to 1.4 as disclosed in applicants' specification at page 15, line 16 as well as elsewhere in the description. As a consequence of this amendment the sphericity mentioned in claim 2 has been deleted as unnecessary (already included in claim 1 from which it depends) and the upper value in claim 9 has been adjusted to 1.4.

Claim 5, indicated to be allowable in the Official Action, is revised to incorporate the subject matter of amended claim 1 and thus claim 5 is an independent process claim which is allowable for the reasons already appreciated by the examiner.

Spherical tetragonal barium titanate particles with a perovskite crystal structure of the present invention as defined in the above-amended claims, have an average particle diameter of 0.05 to 0.5 μm , a particle size distribution σ_g of not less than 0.70, a ratio of Ba to Ti of 0.99:1 to 1.01:1 and a sphericity (maximum diameter/minimum diameter) of 1.0 to 1.4.

The object of this invention is to provide spherical tetragonal barium titanate particles which are free from agglomeration, and can exhibit an excellent dispersibility as well as a high denseness, high purity and excellent permittivity properties.

More specifically, the spherical tetragonal barium titanate particles of the invention are fine tetragonal particles having a Ba/Ti ratio of 0.99 to 1.01 and, therefore,

can exhibit excellent dispersibility and permittivity properties, and are suitable for the production of multi-layered ceramic capacitors having a higher permittivity constant and a lower temperature dependency.

Claims 1, 2, 9 and 11 have attracted a rejection of alleged "obviousness" over the disclosures of Japan 5-330824, Begg et al or Ikawa et al. Applicants respectfully disagree with the examiner's assertions, particularly in light of the claim amendments presented above as well as the attached evidentiary declaration of Mr. Kurokawa made March 12, 2004. The data included in this declaration are discussed in the remarks that follow.

Japanese Patent Application Laid-Open (KOKAI) No.5-330824(1993) discloses a method of subjecting a titanium compound and a barium compound to wet-reaction by adding an aqueous hydrogen peroxide solution thereto. However, the obtained barium titanate particles exhibit a cubic crystal system and, therefore, must be calcined in order to transform them into tetragonal barium titanate particles.

As seen from Mr. Kurokawa's Declaration, the obtained calcined particles were measured by an X-ray diffraction method, and it was confirmed that a peak attributed to a substance other than BaTiO_3 (probably BaTi_3O_7) was observed. Thus, the obtained calcined particles are not phase particles and, therefore, fail to show excellent permittivity properties.

As seen from the X-ray diffractions, since peaks attributed to substances other than BaTiO_3 are recognized, the obtained particles do not have a single crystal structure.

This evidence also shows that the particles in Experiments 1 to 4 are different from the spherical tetragonal barium titanate particles of the present invention.

Further, as seen from the measured permittivity constant ϵ , the permittivity constant ϵ of each of the above dielectric composition obtained from the particles in Experiments 1 to 4 is lower than that of the dielectric composition produced from the barium titanate obtained in Example 1 of the present invention.

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Accordingly, one of ordinary skill in the art cannot forecast spherical tetragonal barium titanate particles with a perovskite crystal structure from Japanese Patent Application Laid-open (KOKAI) 5-330824.

The same holds true for the additionally applied references, Begg et al: "Effect of particle size on the room-temperature crystal structure of barium titanate" pp3186-92, J.Am. Ceram. Soc., 77 3186-92 (1994), as well as Ikawa et al: "Size effect on low temperature phase transformations in BaTiO₃ fine powders analyzed by heat capacity" Dept. of App. Chemistry Book 1 pp.447-450.

For the above reasons it is respectfully submitted that claims 1, 2, 5, 9, and 11 define inventive subject matter and are in condition for allowance. Favorable action is solicited. Should the examiner require further information, please contact the undersigned by telephone.

Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

OKINAKA ET AL.

SERIAL NO. 09/986,657

GROUP ART UNIT: 1754

FILED: November 9, 2001

EXAMINER: S. BOS

FOR: SPHERICAL TETRAGONAL BARIUM
TITANATE PARTICLES AND
PROCESS FOR PRODUCING THE SAME

DECLARATION UNDER 37 C.F.R. 1.132

HONORABLE COMMISSIONER OF PATENTS & TRADEMARKS

WASHINGTON, D.C. 20231

SIR:

Now comes Haruki KUROKAWA, a citizen of Japan, and a resident of Rumieru II Koihonmachi 305, 11-11, Koihonmachi 3-chome, Nishi-ku, Hiroshima-shi, Hiroshima-ken, Japan, who declares and says that:

1. I graduated from Department of Applied Chemistry, Faculty of Technology, Keio University in March, 1984.

2. I am currently employed by TODA KOGYO CORPORATION since April, 1986.

3. I am familiar with the work related to U.S. Patent Application, Serial No. 09/986,657, and am a co-inventor of U.S. Patent Publication Nos. US-2002-0155323-A1 and US-2003-0136473-A1.

4. Under my control and supervision the following experiments were conducted:

Experiment 1 (Example 1 of Japanese Patent Application Laid-open (KOKAI) 5-330824)

A titanium hydroxide gel obtained by hydrolyzing an aqueous titanium tetrachloride solution (produced by Osaka Titanium Co., Ltd.; titanium content: 16.4%) with a 5% aqueous ammonia was filtered and then washed with water to obtain a titanium hydroxide cake (I) having a titanium oxide concentration of 12.3% calculated as the weight by ignition loss.

200 g of the thus obtained titanium hydroxide cake (I) is uniformly dispersed in 654 g of water to obtain an aqueous solution thereof. Then, 221 g of a 30% hydrogen peroxide aqueous solution was added to the thus obtained aqueous titanium hydroxide solution. At this time, it was confirmed that the molar ratio of hydrogen peroxide to titanium oxide (hereinafter expressed by $[H_2O_2/TiO_2]$ (molar ratio)) contained in the resultant slurry was 6.34, and the titanium oxide concentration in the slurry was 0.312 mol/liter assuming that 70% of the 30% hydrogen peroxide aqueous solution was composed of water.

The thus obtained slurry was uniformly stirred at 60°C for 2 hours to obtain a suspension (II). The resultant suspension was naturally cooled to 40°C, and then mixed with 136 g of barium hydroxide octahydrate in such an amount that the molar ratio of Bi to Ti $[Ba/Ti]$ was 1.4. The resultant mixture was heated to 100°C for 0.5 hour while flowing

nitrogen therethrough, and then reacted for 4 hours under refluxing.

As a result, it was confirmed that barium titanate produced by the above reaction was in the form of spherical agglomerates composed of primary particles thereof.

Experiment 2 (Example 5 of Japanese Patent Application Laid-open (KOKAI) 5-330824 corresponding to Comparative Example 9 in our specification)

A titanium hydroxide gel obtained by hydrolyzing an aqueous titanium tetrachloride solution (produced by Osaka Titanium Co., Ltd.; titanium content: 16.4%) with a 5% aqueous ammonia was filtered and then washed with water to obtain a titanium hydroxide cake (I) having a titanium oxide concentration of 12.3% calculated as the weight by ignition loss.

200 g of the thus obtained titanium hydroxide cake (I) is uniformly dispersed in 80 g of water to obtain an aqueous solution thereof. Then, 221 g of a 30% hydrogen peroxide aqueous solution was added to the thus obtained aqueous titanium hydroxide solution. At this time, it was confirmed that the molar ratio of hydrogen peroxide to titanium oxide (hereinafter expressed by $[H_2O_2/TiO_2]$ (molar ratio)) contained in the resultant slurry was 6.35, and the titanium oxide concentration in the slurry was 0.75 mol/liter assuming that 70% of the 30% hydrogen peroxide aqueous solution was composed of water.

The thus obtained slurry was uniformly stirred at 20°C for 2 hours to obtain a suspension (III). The resultant suspension was naturally cooled to 40°C, and then mixed with 194 g of barium hydroxide octahydrate in such an amount that the molar ratio of Bi to Ti [Ba/Ti] was 2.0. The resultant mixture was heated to 100°C for 0.5 hour while flowing nitrogen therethrough, and then reacted for 4 hours under refluxing.

As a result, it was confirmed that barium titanate produced by the above reaction was in the form of spherical agglomerates composed of primary particles thereof.

Experiment 3 (Begg et al: "Effect of particle size on the room-temperature crystal structure of barium titanate" pp3186-92, J.Am. Ceram. Soc., 77 3186-92 (1994))

0.03 mole each of a hydrolyzed titanium alkoxide precursor and barium hydroxide were added to 30 ml of demineralized/deionized water and placed inside a 71-ml unstirred pressure vessel, heated at 5°C/min to 300°C and held for 5 days. The sample was removed from the vessel after cooling, washed in 100 ml of hot (80°C) demineralized/deionized water to remove the unreacted $\text{Ba}(\text{OH})_2$ and amorphous titanium hydrolysate and later in nitric acid to remove residual BaCO_3 and TiO_2 .

The hydrothermal powder was sintered in an air atmosphere at 800°C for 120 hours and 900°C for 60 hours.

Experiment 4 (Ikawa et al: "Size effect on low temperature phase transformations in BaTiO₃ fine powders analyzed by heat capacity" Dept. of App. Chemistry Book 1 pp.447-450)

The barium titanate powder used was supplied from the Sakai Chemical Industry Co. Ltd. This hydrothermally synthesized powder was spherical and non-ferroelectric. This powder was heated at fixed temperature of 800°C for 4 hours.

Various properties of the obtained products were measured by the following methods.

(1) The average particle diameter of the particles is expressed by the average value of particle diameters of about 350 particles observed on an enlarged photograph obtained by magnifying an electron micrograph ($\times 20,000$) four times in each of longitudinal and transverse directions.

(2) The shape of the barium titanate particles was determined from the above electron micrograph.

(3) The particle size distribution of the barium titanate particles is expressed by the geometrical standard deviation σ_g obtained by the following method.

That is, the major axis diameters of 350 particles observed on the enlarged photograph were measured. The actual major axis diameters and the number of the particles were obtained from the calculation on the basis of the measured values. In logarithmic normal probability paper, the major axis diameters were plotted at regular intervals

on the abscissa axis and the accumulative number (under integration sieve) of particles belonging to each interval of the major axis diameters was plotted on the ordinate axis by a statistical technique. The major axis diameters corresponding to the number of particles of 50% and 84.13%, respectively, were read from the graph, and the geometrical standard deviation (σ_g) was obtained by dividing "major axis diameter (μm) corresponding to the number of particles of 50%" by "major axis diameter (μm) corresponding to the number of particles of 84.13%". The more the geometrical standard deviation nears 1.0, the more excellent the particle size distribution of the particles.

(4) The Ba/Ti ratio was measured by a fluorescent X-ray spectroscopy device "Simultix 12" (manufactured by RIGAKU CO., LTD.).

(5) The specific surface area value was measured by BET method.

(6) The crystal structure of the barium titanate particles was determined from the diffraction peak measured in a region 2θ of 10 to 90° using an X-ray diffraction apparatus "RINT-1100K" (manufactured by RIGAKU DENKI CO., LTD.) (Bulb used: Cu).

Table

Examples and Comparative Examples	Properties of barium titanate particles			
	Shape	Sphericity	Average particle diameter (μm)	Particle size distribution (σ) (-)
Our invention	Spherical	1.0 to 1.4	0.05 to 0.5	≥ 0.70
Experiment 1	Spherical	1.0	0.7	0.65
Experiment 2	Spherical	1.0	0.2	0.62
Experiment 3	Rectangular	1.8	0.23	0.74
Experiment 4	Spherical	1.1	0.2	0.68

Table (continued)

Examples and Comparative Examples	Properties of barium titanate particles		
	BET specific surface area (m^2/g)	Ba/Ti ratio (-)	Crystallinity $[(c/a-1) \times 10^3]$ (-)
Our invention	2 to 30	0.99:1 to 1.01:1	≥ 5
Experiment 1	2.3	0.901	3
Experiment 2	7.5	0.872	2
Experiment 3	2.8	1.002	8
Experiment 4	4.7	0.997	4

The permittivity constant ϵ and permittivity loss $\tan\delta$ of each dielectric composition formed from obtained particles of Experiments 1 to 4 were measured as follows.

Then, 65 g of the thus obtained particles were mixed with 100 g of water, and pulverized and deaggregated using 260 g of 1 mm ϕ zirconia beads in a ball mill for 24 hours, thereby obtaining a slurry. The obtained slurry was mixed with 0.325 g of sodium silicate (water glass #3; 0.143% by weight (calculated as SiO₂) based on the weight of the particles). Thereafter, the slurry was washed with water using a suction filter (Nutsche), and then filtered out and dried, thereby obtaining SiO₂-coated particles. The thus obtained coated particles were calcined at 1,020°C for 3 hours in an electric furnace, thereby obtaining a dielectric composition composed of the particles.

The dielectric composition obtained was pulverized using an attritor with an agate mortar for 5 minutes. The pulverized dielectric composition was mixed with a PVA solution containing "RS2117" (produced by KURARAY CO., LTD.) in an amount of 4% by weight, and the resultant mixture was pulverized using an attritor with an agate mortar for 10 minutes, and then passed through a 500- μ m stainless steel sieve to obtain classified particles. The classified particles were dried in a dryer for 60 minutes.

After drying, 2 g of the resultant classified particles were filled in a 21.1 mm ϕ mold, and press-molded under a

mold pressure of 1 ton/cm² for 3 seconds using a pressing machine.

The obtained molded product was placed on an alumina plate, heated to a temperature of 1,150 to 1,300°C at a temperature rise rate of 100°C/hour in an electric furnace, and then calcined at the same temperature for 4 hours.

The thus calcined product was coated with an Ag paste, and then allowed to stand at 700°C for 2 hours in an electric furnace, thereby obtaining a dielectric single plate having an Ag electrode baked thereon.

The permittivity constant ϵ and permittivity loss $\tan\delta$ of the obtained dielectric single plate were measured at an input signal level of 1 Vrms and a frequency of 1 kHz using a LCR meter ("1kHz/1MHz-Capacitance Meter" manufactured by Hewlett Packard Corp.) while varying the temperature over the range of -55 to 150°C in order to determine the permittivity thereof.

As a result of the measurement, the permittivity constant ϵ of each of the above dielectric composition obtained from each of particles of Experiments 1 to 4 is lower than that of the dielectric composition produced from the barium titanate obtained in Example 1 of our invention.

Remarks

As seen from the above Tables, the particles in Experiments 1 to 4 are different from the spherical tetragonal barium titanate particles of our invention.

Further, as seen from the above, the particles in Experiments 1 to 4 are inferior in permittivity constant ϵ to the spherical tetragonal barium titanate particles of our invention.

For example, as apparent from the X-ray diffraction pattern in Fig 8 of Comparative Example 9 in our specification, which corresponds to Experiment, since peaks attributed to substances other than BaTiO_3 are recognized, the obtained particles do not have a single crystal structure.

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 12/March/2004

Haruki Kurokawa
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